

Surface Modification and Nanojunction Fabrication with Molecular Metal Wires

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14. ABSTRACT Electron transfer has been a core subject in science and technology. This project focuses on the development of molecular wires with metal-metal bonds. The long-term goals of this research team aim for developing devices taking advantage of the unique electron transporting behaviors across the nano-objects. One of the first steps is to tailor the axial ligands for the molecular wires, specifically, to make contact between molecules and the electrode. We have studied diruthenium wires containing axial ligands of tetrathiafulvalene-acetylide , masked diazoniums , olefins, and phosphonate . Binding with sulfur and phosphonate to gold and silica oxide surface will then be possible. We also showed that the properties of metal string complexes with three or more metal atoms can be tuned by equatorial ligands, such as rigid naphthylridylamide , super rigid anthyridines , and sulfur-containing ligands (e.g., pyridylthiazolylamine) and bulky camphorsulfonyl groups to manifest the chirality of metal strings. With replacement of metal cores or chromatographic purification, heterometallic strings can be prepared. Studies show that the ligands perturb the electronic structures and the electron-transport properties of the metal-metal frameworks. Platforms of conductance measurements for single-molecule studies have been developed. Two mini-reviews were published in 2014 on the synthesis of metal strings and on conductance mechanisms.		
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Conductance (<i>Angew. Chem. Int. Ed.</i> 2013 , 52, 2449).	
(2) Conductance of Tailored Molecular Segments: a Rudimentary Assessment by Landauer Formulation (<i>J. Am. Chem. Soc.</i> 2014 , 136, 1832).	
(3) Molecular Split-Ring Resonators Based on Metal String Complexes (<i>J. Phys. Chem. C</i> 2014 , Published on web on January 28, 2014).	
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Abstract

Electron transfer has been a core subject in science and technology. This AOARD project focuses on the development of molecular wires with metal-metal bonds. The long-term goals of this research team aim for developing devices taking advantage of the unique electron transporting behaviors across the nano-objects. One of the first steps is to tailor the axial ligands for the molecular wires, specifically, to make contact between molecules and the electrode. We have studied diruthenium wires containing axial ligands of tetrathiafulvalene-acetylide (*Organometallics* **2012**, *31*, 8591), masked diazoniums (*J. Organomet. Chem.* **2013**, *745*, 93), olefins (*Inorg. Chim. Acta* **2013**, *396*, 144), and phosphonate (*Organometallics* **2013**, *32*, 6461). Binding with sulfur and phosphonate to gold and silica oxide surface will then be possible (*Organometallics* **2013**, *32*, 1129). We also showed that the properties of metal string complexes with three or more metal atoms can be tuned by equatorial ligands, such as rigid naphthylridylamide (*Inorg. Chem. Commun.* **2013**, *38*, 152), super rigid anthryridines (*New J. Chem.* **2012**, *36*, 2340), and sulfur-containing ligands (e.g., pyridylthiazolylamine, *Eur. J. Inorg. Chem.* **2013**, 263), and bulky camphorsulfonyl groups to manifest the chirality of metal strings (*Chem.-Asian J.* **2014**, *9*, accepted). With replacement of metal cores (*Chem. Commun.* **2013**, *49*, 7938) or chromatographic purification (*Chem.-Eur. J.* **2014**, *20*, accepted), heterometallic strings can be prepared. Studies show that the ligands perturb the electronic structures and the electron-transport properties of the metal-metal frameworks. Platforms of conductance measurements for single-molecule studies have been developed (*Angew. Chem. Int. Ed.* **2013**, *52*, 2449; *J. Am. Chem. Soc.* **2014**, *136*, 1832). Two mini-reviews were published in 2014 (*J. Chin. Chem. Soc.* **2014**, *61*, 9–26; **2014**, *61*, 101–114) on the synthesis of metal strings and on conductance mechanisms.

Introduction

The recent progress of molecular electronics has been manifested by the discovery of molecular properties such as conductance, rectification, and negative differential resistance. Further advancement requires a comprehensive understanding of the I - V characteristics to enable the development of molecular wires, voltage-gated switches, and single molecular transistors. Distinguished from other groups who typically concentrate on carbon-based molecules, extended metal atom chains (EMACs) and diruthenium wires ($\text{Ru}_2(\text{ap})_4$ and $\text{Ru}_2(\text{DMBA})_4$) are our focus, where *ap* is 2-anilinopyridinate and DMBA is *N,N*-dimethylbenzaminate. EMACs are strings of metal atoms supported by four ligands which provide multiple pathways to tune the molecular properties. These complexes resemble the electric wires in our macroscopic world as proposed by Cotton's group and demonstrated by the simulation work of Jin's group (*J. Phys. Chem. C* **2010**, *114*, 3641). Hence, EMACs alone or being further hybridized with organic ligands are particularly attractive in the field of molecular electronics. Other than the prototypical pyridylamide ligands, in this project we have developed chiral, asymmetric, and naphthylridylamide ones as well as their derivatives. Preparation and purification of prolonged EMACs and heterometal chains will be challenging (see below).



Metal alkynyl complexes have been considered as building blocks for molecular wires. Diruthenium units prepared in this team are shown efficient electron/hole transport media (recent examples: *J. Am. Chem. Soc.* **2011**, *133*, 15094; *Angew. Chem. Int. Ed.* **2010**, *49*, 954). Our current efforts focus on further functionalization of these compounds to enable their attachment to both metallic, semiconductor (Si) and oxide surfaces through the capping groups thiol, olefin and phosphonate, respectively.

Single-molecule measurements are now a routine task for this team. The resistance values of many of the EMACs have been unraveled. In the past years of this project we developed and reported a novel methodology using a sensitive piezoelectrics to fix the junction spacing for EMACs and to acquire impeccable i - V_{bias} scans for the subsequent analysis. The measurements in electron/hole transporting through the metal-metal bonds are the first step of the exploration of the tailored metal string complexes to become functional devices in the future molecular electronics. Therefore, the development of synthetic strategies that tune the molecular properties is of paramount importance. During the course of this project, this team demonstrated approaches to adjust the properties of EMACs and diruthenium,

including the modification of the ligands which improve the delocalization of unpaired electrons and thus the molecular conductance. The results of these studies are reported by providing the abstract of the corresponding publication.

Results and Discussion:

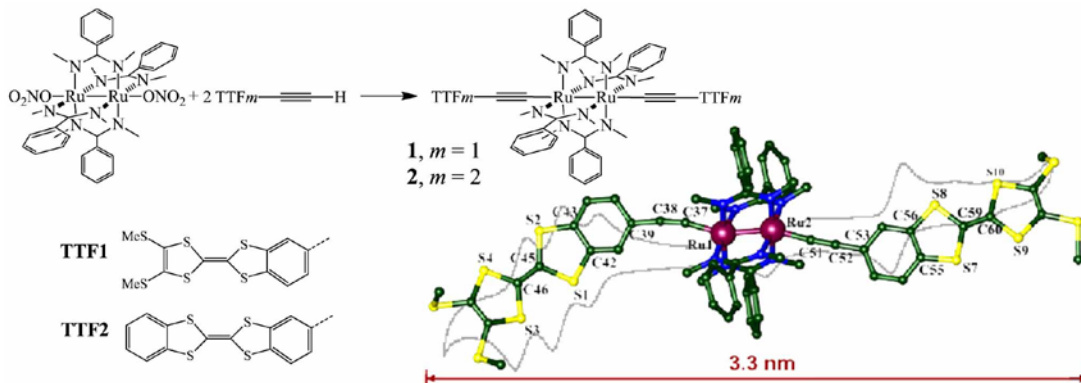
The physical properties of $\text{Ru}_2(\text{ap})_4$ and $\text{Ru}_2(\text{DMBA})_4$ units are perturbed by newly synthesized axial ligands. The metal-metal interactions, in terms of electron transporting through the metal framework or mediated by the Ru_2 moiety are examined. For EMACs, atypical equatorial ligands are prepared. With the help of our recently refined chromatographic methods, heterometallic EMACs are isolated and studied.

1. π -Conjugated Diruthenium Compounds with Tailored Axial Linkers

(1) *Organometallics* **2012**, 31, 8591–8597.

Title: New Linear π -Conjugated Diruthenium Compounds Containing Axial Tetrathiafulvalene-Acetylide Ligands.

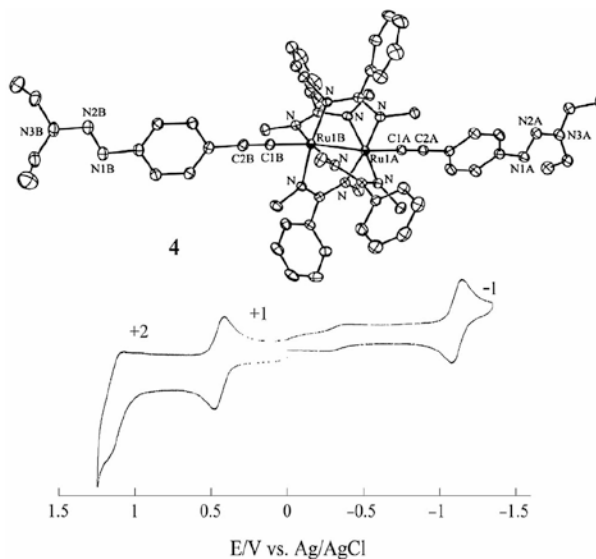
Under the weak base conditions, diruthenium(III) *tetrakis-N,N'*-dimethylbenzaminate (DMBA) nitrate ($\text{Ru}_2(\text{DMBA})_4(\text{NO}_3)_2$) reacted with electroactive tetrathiafulvalene acetylene ligands, $\text{HC}\equiv\text{C}$ -TTF1 (5-ethynyl-2-(4,5-dimethyl-1,3-dithiol-2-ylidene)benzo[*d*][1,3]dithiole) and $\text{HC}\equiv\text{C}$ -TTF2 (2-(5-ethynylbenzo[*d*][1,3]dithiol-2-ylidene)-benzo[*d*][1,3]dithiole), to afford new compounds *trans*- $\text{Ru}_2(\text{DMBA})_4(\text{C}\equiv\text{C}$ -TTF1)₂ (**1**) and *trans*- $\text{Ru}_2(\text{DMBA})_4(\text{C}\equiv\text{C}$ -TTF2)₂ (**2**), respectively. The *trans* orientation and the planar nature of the ethynyltetrathiafulvalene ligands around the $\text{Ru}_2(\text{III,III})$ core were supported by the single-crystal X-ray diffraction study of compound **1**. Both compounds **1** and **2** and their TTF ligand precursors were characterized with the spectroscopic and voltammetric techniques, which revealed a minimal electronic interaction between the two TTF moieties within the same compound. The electronic structure of *trans*- $\text{Ru}_2(\text{DMBA})_4(\text{C}\equiv\text{C}$ -TTF)₂ was analyzed based on a DFT calculation of a model compound, and the resultant distribution of valence MOs is consistent with the voltammetric results.



(2) *J. Organomet. Chem.* **2013**, 745, 93–97.

Title: Diruthenium Acetylide Compounds with Masked Diazonium Capping Groups.

Reported in this contribution are the synthesis and characterization of the following diruthenium arylacetylide compounds containing dialkyltriazene capping groups: $\text{Ru}_2(\text{ap})_4-(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{N}_3\text{Et}_2)$ (**2**), $\text{Ru}_2(\text{ap})_4-(\text{C}\equiv\text{C}-3-\text{C}_6\text{H}_4-\text{N}_3\text{Et}_2)$ (**3**), and *trans*- $[\text{Ru}_2(\text{DMBA})_4](\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{N}_3\text{Et}_2)_2$ (**4**), where *ap* is 2-anilinopyridinate and DMBA is *N,N*-dimethylbenzaminate. Compounds **2** and **3** were prepared by the addition of diethylamine to the diazonium intermediate,

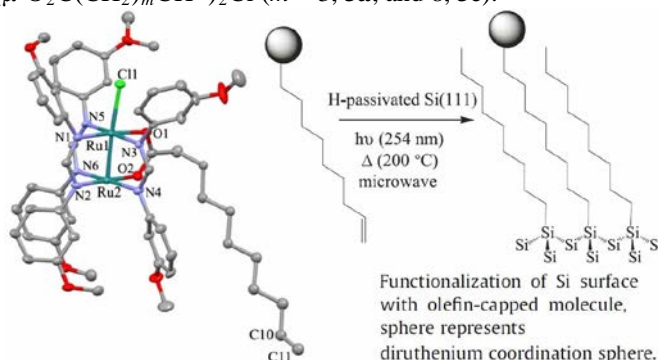


$\text{Ru}_2(\text{ap})_4-(\text{C}\equiv\text{C}-3/4-\text{C}_6\text{H}_4-\text{N}_2^+)$, under basic conditions, and compound **4** was synthesized from $\text{Ru}_2(\text{DMBA})_4(\text{NO}_3)_2$ and $\text{HC}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{N}_3\text{Et}_2$ under weakly basic conditions. An X-ray study of **4** provided a unique structural example of inorganic compounds bearing dialkyl-etriazene functional groups, and revealed a minimal alteration in the first coordination sphere of Ru_2 core upon the attachment of dialkyl-etriazene caps. Similar to previously reported diruthenium compounds, **2**, **3** and **4** display rich redox chemistry with a reversible diruthenium oxidation and reduction, as well as an oxidation of the triazene group to a radical.

(3) *Inorg. Chim. Acta* **2013**, 396, 144–148.

Title: New Diruthenium(II,III) Compounds Bearing Terminal Olefin Groups.

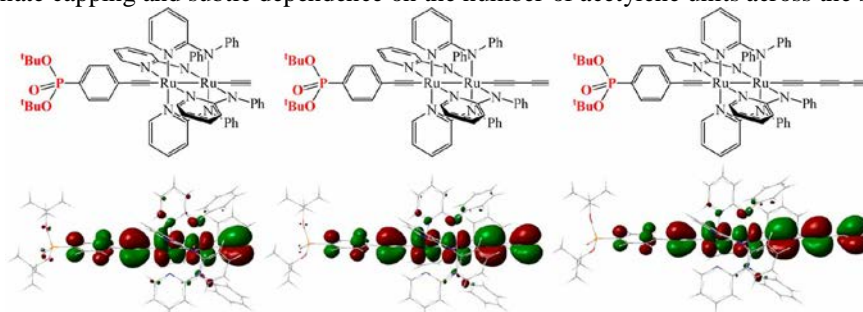
The reaction between $\text{Ru}_2(\text{DmAniF})_3(\text{OAc})\text{Cl}$ (DmAniF is *N,N'*-di(*m*-methoxyphenyl)formamidinate) and $\text{HO}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2$ ($m = 3, 4$ and 8) under reflux afforded new diruthenium species $\text{Ru}_2(\text{DmAniF})_3(\text{O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)\text{Cl}$ ($m = 3$, **1a**; **4**, **1b**; and **8**, **1c**). The structure of **1c** is presented below. Similarly, the reaction between *cis*- $\text{Ru}_2(\text{DmAniF})_2(\text{OAc})_2\text{Cl}$ and $\text{HO}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2$ resulted in $\text{Ru}_2(\text{DmAniF})_2(\text{O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH}_2)_2\text{Cl}$ ($m = 3$, **2a**; and **8**, **2c**). Compounds **2** subsequently underwent an olefin ring closing metathesis reaction catalyzed by $(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru}(=\text{CHPh})$ to afford the dimerized compounds $\text{Ru}_2(\text{DmAniF})_2(\mu-\text{O}_2\text{C}(\text{CH}_2)_m\text{CH}=\text{CH})_2\text{Cl}$ ($m = 3$, **3a**; and **8**, **3c**).



(4) *Organometallics* **2013**, 32, 6461–6467.

Title: New Diruthenium Bis-Alkynyl Compounds as Potential Ditolip Linkers.

The reaction between $\text{Ru}_2(\text{ap})_4-\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{O}^t\text{Bu})_2$ and LiC_2X afforded *trans*- $\text{XC}_2-\text{Ru}_2(\text{ap})_4-\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{O}^t\text{Bu})_2$, where X is $-\text{SiMe}_3$ (**1**), $-\text{C}_2\text{SiMe}_3$ (**2**), $-\text{C}_4\text{H}$ (**3**), or $-\text{C}_6\text{H}_4\text{C}_2\text{SiMe}_3$ (**4**). Compound **5**, *trans*- $(^t\text{BuO})_2(\text{O})\text{P}-\text{C}_6\text{H}_4-4-\text{C}\equiv\text{C}-\text{Ru}_2(\text{ap})_4-\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{SC}_2\text{H}_4-\text{SiMe}_3$, was obtained from the reaction between $\text{Ru}_2(\text{ap})_4-\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{SC}_2\text{H}_4\text{SiMe}_3$ and excess $\text{LiC}\equiv\text{C}-4-\text{C}_6\text{H}_4-\text{P}(\text{O})(\text{O}^t\text{Bu})_2$. Compounds **1–5** were characterized by elemental analysis, HR-*n*ESI-MS, voltammetric and spectroscopic techniques, and the X-ray diffraction study of **2**. The electronic structures of the homologous series **1–3** were investigated using DFT calculations, which revealed both the retention of key features of Ru_2 electronic structure upon the introduction of phosphonate capping and subtle dependence on the number of acetylene units across the series.

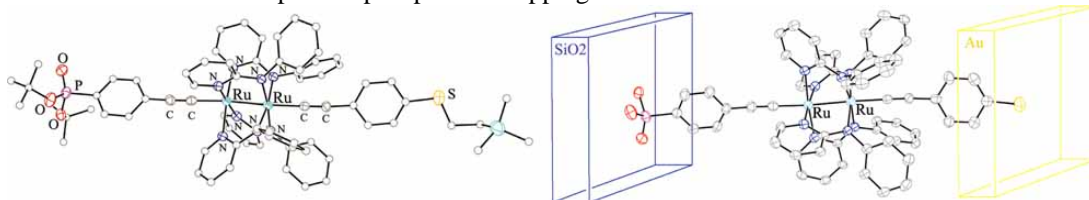


(5) *Organometallics* **2013**, 32, 1129–1132.

Title: Diruthenium Alkynyl Compounds with Phosphonate Capping Groups.

The reaction between $\text{Ru}_2(\text{ap})_4\text{Cl}$ and $\text{LiC}\equiv\text{C}-4-\text{Ph}-\text{P}(\text{O})(\text{O}^t\text{Bu})_2$ afforded $\text{Ru}_2(\text{ap})_4-\text{C}\equiv\text{C}-4-\text{Ph}-\text{P}(\text{O})(\text{O}^t\text{Bu})_2$ (**1**), which was further reacted with $\text{LiC}\equiv\text{C}-4-\text{Ph}-\text{S}(\text{CH}_2)_2\text{SiMe}_3$ to yield *trans*-(4- $\text{Me}_3\text{Si}(\text{CH}_2)_2\text{S}-\text{Ph}-\text{C}\equiv\text{C}$)- $\text{Ru}_2(\text{ap})_4-\text{C}\equiv\text{C}-4-\text{Ph}-\text{P}(\text{O})(\text{O}^t\text{Bu})_2$ (**2**).

trans-Ru₂(DMBA)₄(C≡C-4-Ph-P(O)(O^tBu)₂)₂ (**3**) was obtained from the reaction between Ru₂(DMBA)₄(NO₃)₂ and either HC≡C-4-Ph-P(O)(O^tBu)₂ in the presence of Et₃N or LiC≡C-4-Ph-P(O)(O^tBu)₂. Compounds **1–3** were characterized by HR-MS, X-ray diffraction, and voltammetric techniques, which revealed the retention of essential characteristics in molecular and electronic structures upon the phosphonate capping.

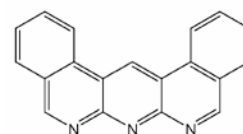


2. Extended Metal-Atom Chains: Novel Equatorial Ligands and Heterometallic Chains

(1) *New J. Chem.* **2012**, 36, 2340–2346.

Title: Transition Metal Complexes of a Super Rigid Anthridine Ligand: Structural, Magnetic and DFT Studies.

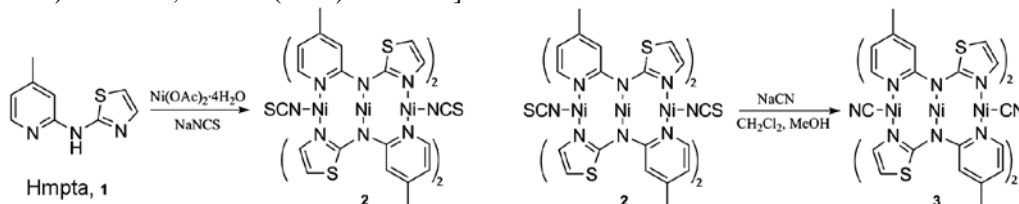
Transition metal complexes of iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) with a plane, super rigid ligand (see Figure), 1,13,14-triaza-dibenzo[*a,j*]anthracene (L), [M₂L₄](ClO₄)₄ (M = Fe, Co, Ni, Cu, Zn), were synthesized and their magnetic properties were studied. All complexes are dinuclear, tetracationic complexes bridged by four tridentate ligands. In a complex each L coordinates to two metal atoms with two nitrogen atoms chelating to one metal and the third nitrogen atom mono-coordinating to another metal. Crystal structure analysis indicated that the molecular structures of the five complexes are essentially the same despite significant distortion from the Jahn–Teller effect of the copper complex. The Cu–Cu distance is 2.907(1) Å, and all other M–M distances are ca. 3.3 Å. Antiferromagnetic couplings were observed for the Fe, Co, Ni and Cu complexes. The exchange parameters were *J* = –6 and –129 cm^{–1} for Ni and Cu complexes, respectively. The mechanism was discussed by spin-polarization, superexchange coupling and DFT calculations. The *J* value obtained from the density functional B3LYP calculations is in good agreement with the experimentally determined value.



(2) *Eur. J. Inorg. Chem.* **2013**, 263–268.

Title: Synthesis, Structure, Magnetism, and Single Molecular Conductance of Linear Trinickel String Complexes with Sulfur-Containing Ligands.

Synthesized herein is an asymmetric ligand of sulfur-containing Hmpta (4-methylpyridylthiazolyl amine, **1**) and two linear trinickel EMACs, [Ni₃(mpta)₄(NCS)₂] (**2**) and [Ni₃(mpta)₄(CN)₂] (**3**). Within the trinickel framework, the two terminal high-spin (*S* = 1) Ni ions are strongly coupled antiferromagnetically (*J* = –91 cm^{–1} in **2** and –79 cm^{–1} in **3**). The axial CN[–] ligand is basic and strongly pulls the terminal Ni ions away from the central Ni ion, resulting in the Ni–Ni bond lengths (ca. 2.52 Å) longer than those in **2** (ca. 2.47 Å). The lengthening of the Ni–Ni bond lengths causes **3** to exhibit weaker antiferromagnetic interactions and lower single molecular conductance [*R* = 11.1 (± 3.9) MΩ for **3**; *R* = 7.1 (± 1.5) MΩ for **2**].

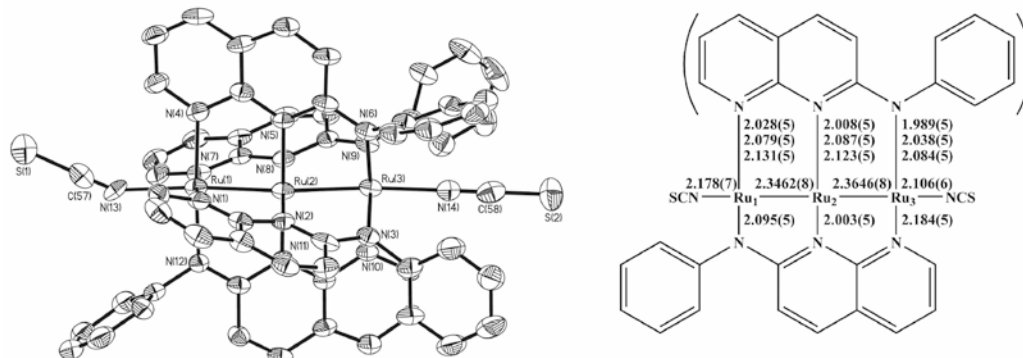


(3) *Inorg. Chem. Commun.* **2013**, 38, 152–155.

Title: A Novel Triruthenium Metal String Complex with Naphthylridylamide Ligand: Synthesis, Structure, Magnetism, and Molecular Conductance.

A triruthenium metal string, [Ru₃(npa)₄(NCS)₂][PF₆] (**1**), supported by naphthylridylamide (npa) ligands was successfully synthesized and is reported in this work. X-ray single crystal analysis shows that compound **1** exhibits a nonlinear [Ru₃]⁷⁺ backbone (∠ = 170.26(3)°) with long Ru–Ru bond lengths (2.3554(8) Å). The long Ru–Ru distances observed for **1** decrease the Ru–Ru interactions and electric conductance. Magnetic measurements indicate that compound **1** is in an *S* =

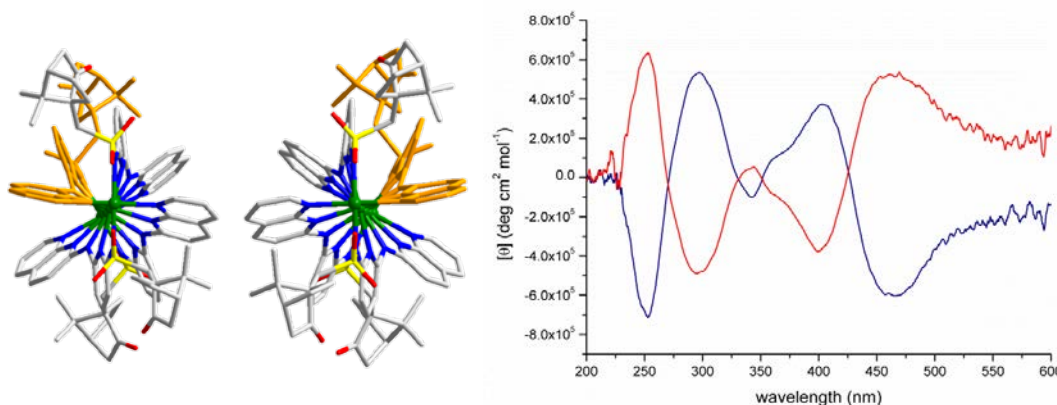
1/2 state. DFT calculations suggest that this unpaired electron occupies the π^* orbital which is stabilized by π -acid NCS⁻ ligands and thus weakening the Ru–Ru π interaction.



(4) *Chem.–Asian J.* **2014**, 9, Accepted.

Title: Chirality Control of Quadruple Helixes of Metal Strings by Peripheral Chiral Ligands.

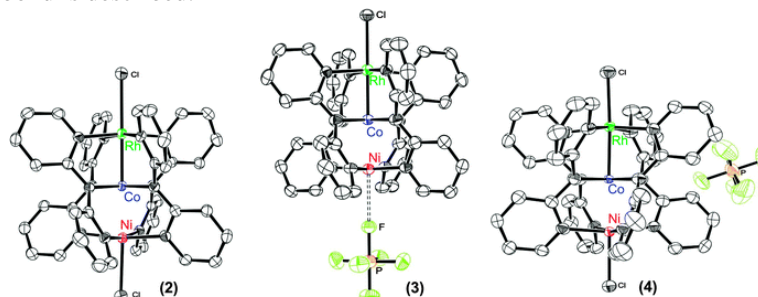
Novel chiral pentadentate ligands with naphthyridine and camphorsulfonyl groups have been designed and used to control the chirality of quadruple helixes of metal strings directly. Δ -[Ni₅((-)-camnpda)₄] and Λ -[Ni₅((+)-camnpda)₄] are reported.



(5) *Chem. Commun.* **2013**, 49, 7938–7940.

Title: Facile Synthesis of Heterotrimetallic Metal–string Complex [NiCoRh(dpa)₄Cl₂] through Direct Metal Replacement.

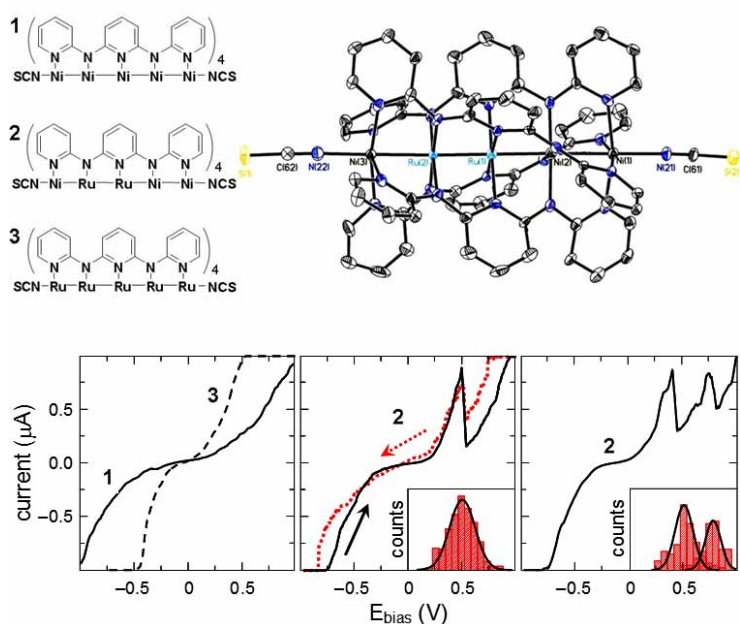
This *Communication* provides a practical strategy for the synthesis of heterotrimetallic extended metal atom chains with supported dpa⁻ ligands. The transformation of the CoCoRh to a NiCoRh trinuclear complex can be achieved by direct metallic replacement. Furthermore, the first (CoRh)⁴⁺ metal–metal bond is described.



(6) *Chem.–Eur. J.* **2014**, 20, Accepted.

Title: The First Heteropentannuclear Extended Metal-Atom Chain: [Ni⁺–Ru₂⁵⁺–Ni²⁺–Ni²⁺(tri-pyridyldiamido)₄(NCS)₂].

This study develops the first heteropentametal EMAC in which a string of nickel cores is incorporated with a diruthenium unit to tune the molecular properties. Spectroscopic, crystallographic, and magnetic characterizations show the formation of a fully delocalized Ru_2^{5+} unit. This $[\text{Ru}_2]$ -containing EMAC exhibits the single-molecule conductance 4-fold superior to that of the pentanickel complex and results in features of NDR (negative differential resistance) which are unobserved for its analogues of pentanickel and pentaruthenium EMACs. A plausible mechanism for the NDR behavior is proposed for this diruthenium-modulated EMAC.

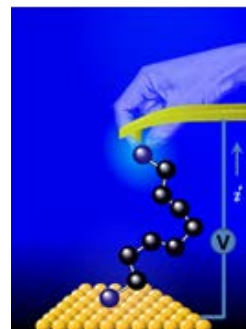


3. Single-Molecule Conductance

- (1) *Angew. Chem. Int. Ed.* **2013**, 52, 2449–2453.

Title: Tactile-Feedback Stabilized Molecular Junctions for the Measurements of Molecular Conductance.

One of the key hurdles to gain comprehensive perspective on molecular electronics is the inadequacy of reliable acquisition of i - V traces for single molecules. This is because contemporarily the molecular junctions are unstable and last shorter than tenths of seconds. In this study, by introducing an additional control of force to the measurement platform, the junction lifetime becomes typically hundreds of seconds, sufficiently long for consecutive i - V scans and for the monitoring of time-dependent behaviors. New insights about single molecules are found, such as the study of single-molecule behaviors from truly one molecular junction, as opposed to those from collective dataset from many junctions with millisecond lifetime. Information of single-molecule conductance as a function of the applied force can be obtained. The results also reveal which of *gauche* or *trans* conformers is more conductive, a controversial issue in molecular electronics.



- (2) *J. Am. Chem. Soc.* **2014**, 136, 1832–1841.

Title: Conductance of Tailored Molecular Segments: a Rudimentary Assessment by Landauer Formulation.

One of the strengths of molecular electronics is the synthetic ability of tuning the electric properties by the derivatization and reshaping of the functional moieties. However, after the quantitative measurements of single-molecule resistance became available, it was soon apparent that the assumption of negligible influence of the headgroup–electrode contact on the molecular resistance was oversimplified. Due to the measurement scheme of the metal–molecule–metal configuration, the contact resistance is always involved in the reported values. Consequently the electrical behavior of the tailored molecular moiety can only be conceptually inferred by the tunneling decay constant (β_n in $R_{\text{measured}} = R_{n=0}e^{\beta_n N}$, where N is the number of repeated units), available only for compounds with a homologous series. This limitation hampers the exploration of novel structures for molecular devices. Based on Landauer formula, we propose that the

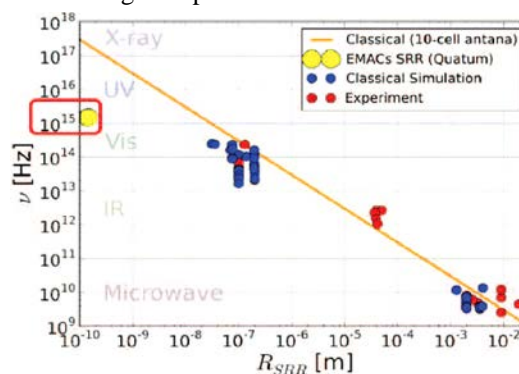


single-molecule resistance of the molecular backbones can be extracted. This simplified evaluation scheme is cross-examined by electrode materials of Au, Pd, and Pt, and by anchoring groups of thiol ($-\text{SH}$), nitrile ($-\text{CN}$), and isothiocyanate ($-\text{NCS}$). The resistance values of molecular backbones for polymethylenes ($n = 4, 6, 8$, and 10), and phenyl ($-\text{C}_6\text{H}_4-$) moieties are found independent of the anchoring groups and electrode materials. The finding justifies the proposed approach that the resistance of functional moieties can be quantitatively evaluated from the measured values even for compounds without repeated units.

(3) *J. Phys. Chem. C* **2014**, Published on web on January 28, 2014.

Title: Molecular Split-Ring Resonators Based on Metal String Complexes.

EMACs is a family of molecules that consist of a linear chain of directly bonded metal atoms embraced helically by four multidentate organic ligands. These four organic ligands are usually made up of repeating pyridyl units, single-nitrogen-substituted heterocyclic annulenes, bridged by independent amido groups. Here, in this study, we show that these heterocyclic annulenes are actually nanoscale molecular split-ring resonators (SRRs) that can exhibit simultaneous negative electric permittivity and magnetic permeability in the UV-vis region. Moreover, a monolayer of self-assembled EMACs is a periodic array of molecular SRRs which can be considered as a negative refractive index material. In the molecular scale, where the quantum-size effect is significant, we apply the tight-binding method to obtain the frequency-dependent permittivity and permeability of these molecular SRRs with their tensorial properties carefully considered.



Concluding Remarks:

We have prepared for Ru_2 wires novel *bis*-alkynyl axial derivatives with capping groups of tetrathiafulvalene-acetylide, diazoniums, olefins, and phosphonates. Attachment of the former compounds to both H-passivated silicon and oxide (silica) surfaces and subsequent device fabrication are being pursued. For EMACs, starting from the prototypical oligo- α -pyridylamine, we have developed new family members of equatorial ligands, such as naphthyridine-modulated, super-rigid anthryridines, sulfur-incorporated thiazolyl, and bulky camphorsulfonyl-decorated ones. Excitingly, chiral EMACs are isolated for the first time and the hetrometallic EMAC with Ru_2 core, $[\text{Ni}-(\text{Ru}_2)-\text{Ni}-\text{Ni}]$, exhibits interesting i-V behaviors of NDR (negative differential resistance). We now can quantitatively obtain single-molecule conductance with a good control over the force applied to the molecular junction such that the molecular junction is less damaged. Therefore, we will be able to carry out conductance studies for the aforementioned molecules, particularly the Ru_2 wires which are able to anchor on hydrogen-passivated silica, silica oxides, and gold surface for the next-stage studies of semiconductor-molecule-metal configurations.

List of Publications:

a) papers published in peer-reviewed journals,

1. "New Linear π -Conjugated Diruthenium Compounds Containing Axial Tetrathiafulvalene-Acetylide Ligands",
Cai, X.-M.; Zhang, X.-Y.; Savchenko, J.; Gao, Z.; Ren, T.*; Zuo, J.-L.* *Organometallics* **2012**, *31*, 8591–8597.
2. "Diruthenium Acetylide Compounds with Masked Diazonium Capping Groups",
Cummings, S. P.; Fanwick, P. E.; Savchenko, J.; Ren, T.* *J. Organomet. Chem.* **2013**, *745*, 93–97.
3. "New Diruthenium (II,III) Compounds Bearing Terminal Olefin Groups",
Savchenko, J.; Fanwick, P. E.; Hope, H.; Gao, Y.; Yerneni, C. K.; Ren, T.* *Inorg. Chim. Acta* **2013**, *396*, 144–148.
4. "Diruthenium Alkynyl Compounds with Phosphonate Capping Groups",
Cummings, S. P.; Savchenko, J.; Fanwick, P. E.; Kharlamova, A.; Ren, T.* *Organometallics* **2013**, *32*, 1129–1132.

5. "New Diruthenium Bis-Alkynyl Compounds as Potential Ditopic Linkers", Savchenko, J.; Cao, Z.; Natoli, S. N.; Cummings, S. P.; Prentice, B. M.; Fanwick, P. E.; Ren, T.* *Organometallics* **2013**, 32, 6461–6467.
 6. "Transition Metal Complexes of a Super Rigid Anthryridine Ligand: Structural, Magnetic and DFT Studies", Wang, W.-Z.; Hsieh, C.-L.; Ismayilov, R. H.; Hsu, C.-H.; Liu, I. P.-C.; Liu, Y.-H.; Lee, G.-H.; Peng, S.-M.* *New J. Chem.* **2012**, 36, 2340–2346.
 7. "Synthesis, Structure, Magnetism, and Single Molecular Conductance of Linear Trinickel String Complexes with Sulfur-Containing Ligands", Yang, C.-C.; Liu, I. P.-C.; Hsu, Y.-J.; Lee, G.-H.; Chen, C.-h.; Peng, S.-M.* *Eur. J. Inorg. Chem.* **2013**, 263–268.
 8. "Tactile-Feedback Stabilized Molecular Junctions for the Measurements of Molecular Conductance", Chen, I.-W. P.; Tseng, W.-H.; Gu, M.-W.; Su, L.-C.; Hsu, C.-H.; Chang, W.-H.; Chen, C.-h.* *Angew. Chem. Int. Ed.* **2013**, 52, 2449–2453.
 9. "A Novel Triruthenium Metal String Complex with Naphthylridylamide Ligand: Synthesis, Structure, Magnetism, and Molecular Conductance", Tsai, C.-S.; Liu, I. P.-C.; Tien, F.-W.; Lee, G.-H.; Yeh, C.-Y.; Chen, C.-h.; Peng, S.-M. *Inorg. Chem. Commun.* **2013**, 38, 152–155.
 10. "Facile Synthesis of Heterotrimetallic Metal–String Complex [NiCoRh(dpa)₄Cl₂] through Direct Metal Replacement", Cheng, M.-C.; Mai, C.-L.; Yeh, C.-Y.; Lee, G.-H.; Peng, S.-M.* *Chem. Commun.* **2013**, 49, 7938–7940.
 11. "Conductance of Tailored Molecular Segments: a Rudimentary Assessment by Landauer Formulation", Huang, M.-J.; Hsu, L.-Y.; Fu, M.-D.; Chuang, S.-T.; Tien, F.-W.; Chen, C.-h.* *J. Am. Chem. Soc.* **2014**, 136, 1832–1841.
 12. "Transitions between Electron Transporting Mechanisms in Molecular Junctions and Transistors", Kuo, C.-T.; Su, L.-C.; Chen, C.-h.* *J. Chin. Chem. Soc.* **2014**, 61, 101–114. (Invited Mini-Review, Special Issue for the 60th Anniversary of *J. Chin. Chem. Soc.*)
 13. "A Journey of Metal-Metal Bonding beyond Cotton's Quadruple Bonds", Hua, S.-A.; Tsai, Y.-C.*; Peng, S.-M.* *J. Chin. Chem. Soc.* **2014**, 61, 9–26. (Invited Mini-Review, Special Issue for the 60th Anniversary of *J. Chin. Chem. Soc.*)
 14. "The First Heteropentannuclear Extended Metal-Atom Chain: [Ni⁺–Ru₂⁵⁺–Ni²⁺–Ni²⁺(tripyriddy diamido)₄(NCS)₂]", Huang, M.-J.; Hua, S.-A.; Fu, M.-D.; Huang, G.-C.; Yin, C.; Ko, C.-H.; Kuo, C.-K.; Hsu, C.-H.; Lee, G.-H.; Ho, K.-Y.; Wang, C.-H.; Yang, Y.-W.; Chen, I.-C.*; Peng, S.-M.*; Chen, C.-h.* *Chem.–Eur. J.* **2014**, 20, Accepted on February 11.
 15. "Molecular Split-Ring Resonators Based on Metal String Complexes", Shen, Y.; Ko, H.-Y.; Ai, Q.; Peng, S.-M.; Jin, B.-Y.* *J. Phys. Chem. C* **2014**, Published on web on January 28, 2014.
 16. "Chirality Control of Quadruple Helixes of Metal Strings by Peripheral Chiral Ligands", Yu, C.-H.; Kuo, M.-S.; Chuang, C.-Y.; Lee, G.-H.; Jin, B.-Y.; Peng, S.-M.* *Chem.–Asian J.* **2014**, 9, Accepted on January 23.
- b) papers published in peer-reviewed conference proceedings,
 - c) papers published in non-peer-reviewed journals and conference proceedings,
 - d) conference presentations without papers,
 - e) manuscripts submitted but not yet published, and
 - f) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

DD882: There is no material from this project required to fill in Form DD882 (the inventions disclosure form). The inventions disclosure form is submitted in a separate document.

Important Note: If the work has been adequately described in refereed publications, submit an abstract as described above and refer the reader to your above List of Publications for details. If a full report needs to be written, then submission of a final report that is very similar to a full length journal article will be sufficient in most cases. This document may be as long or as short as needed to give a fair account of the work performed during the period of performance. There will be variations depending on the scope of the work. As such, there is no length or formatting constraints for the final report. Keep in mind the amount of funding you received relative to the amount of effort you put into the report. For example, do not submit a \$300k report for \$50k worth of funding; likewise, do not submit a \$50k report for \$300k worth of funding. Include as many charts and figures as required to explain the work.

Attachments: Publications a2,4, 5, 8, 9, 11, 13, 15 listed above.